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Pair coupling in $p^2 f$ with application to O II

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With 1 figure in the text

SUMMARY

Formulae have been derived for the structure of $p^2 f$ in intermediate pair coupling, and are shown to give an accurate description of O II $2s^2 2p^2 nf$.

Introduction

The configurations O II $2s^2 2p^2 nf$ with $n=4$ and $n=5$ were discovered by Russell (1928) and Edlén (1934, 1935). The measurements, which are due to Fowler (1926) and Mihul (1928), admit of a complete interpretation for $n=4$ only. The levels occur in close pairs, which means that the influence of the exchange integrals $G_k(2p, nf)$ and the spin-orbit integral ζ_{nf} is small and may be neglected in a first approximation. Furthermore, as the terms of the configuration O III $2s^2 2p^2$, ^1S, ^1D, and ^3P, are widely separated, the three groups of pairs built on these separate parents can be treated independently.

Theoretical structure

When the electrostatic integral $F_2(p, f)$ is responsible for an appreciable part of the term structure in $p^2 f$, it should be of interest to study a vector model, in which the azimuthal quantum number L_c of the core and l of the outer electron are coupled to get a resultant L. The coefficients of F_2 may be taken from Racah's (1942) LS-coupling formulae, while the relation $F_2 = F^2(p, f)/75$ used by Condon and Shortley (1935) is being retained. Then the coupling of L to the spin of the core, S_c, will form the pair quantum number K. The corresponding perturbation energy can be derived in analogy with the procedure used by Goudsmit and Humphreys (1928), giving the expression

$$\frac{K(K+1)-L(L+1)-S_c(S_c+1)}{2}\cdot\frac{L(L+1)+L_c(L_c+1)-l(l+1)}{2L(L+1)}\zeta, \qquad (1)$$

where ζ is the splitting factor of the core term and thus for $p^2(^3P)$ is equal to half the spin-orbit integral ζ_p. The results obtained for $p^2 f$ appear in Table 1 under the heading "LS_c coupling".

Table 1. Vector coupling designations and energies for the pairs of p^2f.

Designation					Energy	
L_c	S_c	J_c	L	K	LS_c coupling	$J_c\,l$ coupling
S	0	0	F	3	E_0''	=
D	0	2	H	5	$E_0'+10F_2$	=
		2	G	4	$E_0'-15F_2$	=
		2	F	3	$E_0'-11F_2$	=
		2	D	2	$E_0'+\ 6F_2$	=
		2	P	1	$E_0'+24F_2$	=
P	1	2	G	5	$E_0-\ 5F_2+\zeta$	=
		2	F	4	$E_0+15F_2+\frac{1}{4}\zeta$	$E_0+\zeta+\frac{15}{2}F_2$
		1	G	4	$E_0-\ 5F_2-\frac{1}{4}\zeta$	$E_0-\zeta+\frac{5}{2}F_2$
		2	F	3	$E_0+15F_2-\frac{1}{12}\zeta$	$E_0+\zeta+\frac{11}{2}F_2$
		1	G	3	$E_0-\ 5F_2-\frac{5}{4}\zeta$	$E_0-\zeta-\frac{15}{2}F_2$
		0	D	3	$E_0-12F_2-\frac{2}{3}\zeta$	$E_0-2\zeta$
		2	F	2	$E_0+15F_2-\frac{1}{3}\zeta$	$E_0+\zeta-3F_2$
		1	D	2	$E_0-12F_2+\frac{1}{3}\zeta$	$E_0-\zeta+6F_2$
		2	D	1	$E_0-12F_2+\zeta$	=

All formulae in Table 1 marked = are valid for any value of the ratio F_2/ζ, but in the group belonging to (^3P) each set of pairs with equal quantum number K should satisfy a common secular equation. When this equation is of the second order, as it is for $K=4$ and $K=2$, the known structures for $F_2 \gg \zeta$ and $F_2=0$ determine the solution uniquely:

$$\left.\begin{aligned} (^3P)\,nf\,(4) &= E_0+5F_2 \pm [(10F_2+\tfrac{1}{4}\zeta)^2+\tfrac{15}{16}\zeta^2]^{\frac{1}{2}} \\ (^3P)\,nf\,(2) &= E_0+\tfrac{3}{2}F_2 \pm [(\tfrac{27}{2}F_2-\tfrac{1}{3}\zeta)^2+\tfrac{8}{9}\zeta^2]^{\frac{1}{2}}. \end{aligned}\right\} \qquad (2)$$

On expanding these expressions for the case $F_2 \ll \zeta$ they reduce to those for $J_c\,l$ coupling. Finally one obtains the energies in $J_c\,l$ coupling for the three pairs with $K=3$, belonging to $(^3P_2)$, $(^3P_1)$, and $(^3P_0)$, respectively, from the rule that the centre of gravity of a group of pairs with the same J_c should not depend on F_2. The coefficients of the third-order secular equation for these pairs may then be derived from the vector-coupling expressions for the two extreme cases $F_2 \gg \zeta$ and $F_2 \ll \zeta$.

However, the interval ratio in $p^2(^3P)$ is not well reproduced by the single parameter ζ, mainly because the mutual magnetic interaction $\eta\,(p,p)$ has been neglected. Since configuration interaction and deviation from LS coupling may also influence the interval ratio, the magnetic integrals have been replaced by the following parameters representing the actual intervals,

$$\left.\begin{aligned} (^3P_2)-(^3P_1) &= A, \\ (^3P_2)-(^3P_0) &= B. \end{aligned}\right\} \qquad (3)$$

Table 2. Intermediate-coupling energies for the pairs of $p^2\,(^3P)\,f$ relative to their centre of gravity, E_0.

J_c	L	K	$E-E_0$
2	G	5	$\frac{1}{3}A+\frac{1}{9}B-5F_2$
2	D	1	$\frac{1}{3}A+\frac{1}{9}B-12F_2$
2	F	4	$-\frac{1}{6}A+\frac{1}{9}B+5F_2\pm[(\frac{1}{2}A)^2+\frac{5}{2}AF_2+(10F_2)^2]^{\frac{1}{2}}$
1	G	4	
2	F	2	$-\frac{1}{6}A+\frac{1}{9}B+\frac{3}{2}F_2\pm[(\frac{1}{2}A)^2-\frac{9}{2}AF_2+(\frac{27}{2}F_2)^2]^{\frac{1}{2}}$
1	D	2	
2	F	3	$-\frac{2}{9}B-\frac{2}{3}F_2+x_i{}^a$
1	G	3	
0	D	3	

[a] x_i are the roots of the equation $x^3-px=q$, where p and q are given by the expressions

$$3p=A^2+B^2-AB+(\tfrac{41}{2}A-2B)F_2+589F_2^2,$$

$$27q=-2A^3-2B^3+3A^2B+3AB^2+(-\tfrac{123}{2}A^2+6B^2+111AB)F_2+$$
$$+(1362A+282B)F_2^2+20774F_2^3.$$

By introducing the structure of $p^2\,(^3P)$, referred to the centre of gravity, E_0, and expressed in A and B, viz.,

$$\left.\begin{aligned}(^3P_2)&=E_0+\ \ A/3+\ \ B/9,\\(^3P_1)&=E_0-2A/3+\ \ B/9,\\(^3P_0)&=E_0+\ \ A/3-8B/9,\end{aligned}\right\}\qquad(4)$$

in the $J_c l$-coupling formulae we obtain the modified formulae for intermediate pair coupling given in Table 2.

Observed structure in O II $2s^2 2p^2 nf$

In Fig. 1 the structure of $p^2\,(^3P)\,f$ in intermediate pair coupling has been plotted for O II as a function of F_2. The parameters A and B, taken as constants, have been determined from the observed intervals in the parent term O III $2s^2 2p^2\,{}^3P$, as is shown in Table 3. It appears that the empirical $4f$ levels, which are well established, fit the theory very accurately. The group of $5f$ levels as given in Atomic Energy Levels [Moore-Sitterly, 1949] has been partly revised with the aid of the theoretical relations shown in Fig. 1. The levels are collected in Table 4. Alternative values are given in some cases where the observational data are ambiguous. The accepted values for the electrostatic interaction integrals, $F_2(2p, 4f)=9.94$ cm^{-1} and $F_2(2p, 5f)=5.04$ cm^{-1}, are proportional to n^{-3} within 0.5 %.

The observed $4f'$ levels in O II have been fitted to the formulae for $p^2\,(^1D)\,f$

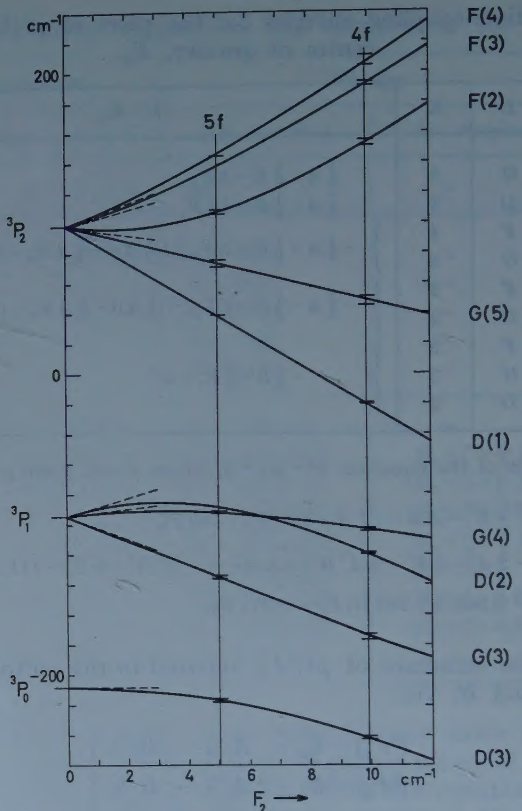

Fig. 1. O II $2s^2\,2p^2\,(^3P)\,nf$, theoretical and observed relative energy levels.

Table 3. O III $2s^2\,2p^2\,^3P$, observed structure and adopted parameter values (cm^{-1}).

Observed interval	Parameter
$^3P_2 - {}^3P_1 = 193.0$ Bowen (1955)	$A = 193.0$
$^3P_2 - {}^3P_0 = 306.8$ Edlén (1934)	$B = 306.6$
$^3P_1 - {}^3P_0 = 113.4$ Edlén (1934)	$B - A = 113.6$

Table 4. O II $2s^2\,2p^2\,(^3P)\,5f$, observed level values (cm^{-1}).

$L\,(K)_J$	Level	$L\,(K)_J$	Level	$L\,(K)_J$	Level
$G\,(5)_{11/2}$	265 925	$F\,(4)_{9/2}$	265 999	$D\,(3)_{7/2}$	265 638
$G\,(5)_{9/2}$	930	$F\,(4)_{7/2}$	999 ?	$D\,(3)_{5/2}$	636
$G\,(4)_{9/2}$	761	$F\,(3)_{7/2}$	991 (985)[a]	$D\,(2)_{5/2}$	767 (762)[a]
$G\,(4)_{7/2}$	763	$F\,(3)_{5/2}$	992 (988)[a]	$D\,(2)_{3/2}$	766 ?
$G\,(3)_{7/2}$	720	$F\,(2)_{5/2}$	963	$D\,(1)_{3/2}$	893
$G\,(3)_{5/2}$	718	$F\,(2)_{3/2}$	960	$D\,(1)_{1/2}$	893

[a] Alternative levels, too low in case of an unperturbed configuration.

Table 5. O II $2s^2 2p^2(^1D)4f$, observed and calculated relative level values. $F_2 = 10.85$ cm^{-1}.

$L(K)$	$E_{\text{obs.}} - E_0'$	$E_{\text{calc.}} - E_0'$	$(E_{\text{obs.}} - E_0')/F_2$	$(E_{\text{calc.}} - E_0')/F_2$
$P(1)$	262.4	260.4	24.18	24
$H(5)$	107.6	108.5	9.92	10
$D(2)$	64.8	65.1	5.97	6
$F(3)$	−121.9	−119.3	−11.24	−11
$G(4)$	−160.2	−162.7	−14.76	−15

in Table 1 with the result shown in Table 5. The value for the electrostatic interaction integral, $F_2(2p, 4f') = 10.85$ cm^{-1}, turns out to be 9 % higher than the value 9.94 cm^{-1} obtained for $F_2(2p, 4f)$. The centroid distance, $E_0' - E_0 = 20\,069$ cm^{-1}, closely agrees with the observed distance between the parent terms, ^1D–$^3P = 20\,065.5$ cm^{-1}.

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